INL/CON-06-11719
PREPRINT

High-Temperature Co-Electrolysis of H_2O and CO_2 for Syngas Production

2006 Fuel Cell Seminar

Carl M. Stoots

November 2006

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

ABSTRACT

Worldwide, the demand for light hydrocarbon fuels like gasoline and diesel oil is increasing. To satisfy this demand, oil companies have begun to utilize oil deposits of lower hydrogen content (e.g., Athabasca Oil Sands). Additionally, the higher contents of sulfur and nitrogen of these resources requires processes such as hydrotreating to meet environmental requirements. In the mean time, with the price of oil currently over $70 / barrel, synthetically-derived hydrocarbon fuels (synfuels) have become economical. Synfuels are typically produced from syngas – hydrogen (H_2) and carbon monoxide (CO) -- using the Fischer-Tropsch process, discovered by Germany before World War II. South Africa has used synfuels to power a significant number of their buses, trucks, and taxicabs.

The Idaho National Laboratory (INL), in conjunction with Ceramatec Inc. (Salt Lake City, USA) has been researching the use of solid-oxide fuel cell technology to electrolyze steam for large-scale nuclear-powered hydrogen production. Now, an experimental research project is underway at the INL to investigate the feasibility of producing syngas by simultaneously electrolyzing steam and carbon dioxide (CO_2) at high-temperature using solid oxide fuel cell technology.

$$H_2O + CO_2 \longrightarrow H_2 + CO + O_2 \cdot \quad (1)$$

The syngas can then be used for synthetic fuel production. This program includes a combination of experimental and computational activities. Since the solid oxide electrolyte material is a conductor of oxygen ions, CO can be produced by electrolyzing CO_2 sequestered from some greenhouse gas-emitting process. Under certain conditions, however, CO can be further electrolysed to produce carbon, which can then deposit on cell surfaces and reduce cell performance. Furthermore, the understanding of the co-electrolysis of steam and CO_2 is complicated by the competing water-gas shift reaction.

Results of experiments and calculations to date of CO_2 and CO_2/H_2O electrolysis will be presented and discussed. These will include electrolysis performance at various temperatures, gas mixtures, and electrical settings. Product gas compositions, as measured via a gas analyser and their relationship to conversion efficiencies will be presented. These measurements will be compared to predictions obtained from a chemical equilibrium/electrolysis model. Better understanding of the feasibility of producing syngas using high-temperature electrolysis will initiate the systematic investigation of nuclear-powered synfuel production as a bridge to the future hydrogen economy and ultimate independence from foreign energy resources.

EXPERIMENTAL

A schematic of the apparatus used for co-electrolysis testing at the INL is shown in Figure 1. A photograph follows in Figure 2. Primary components include gas supply cylinders, nitrogen gas generator, mass-flow controllers, a humidifier, dewpoint measurement stations, temperature and pressure measurement, high temperature furnace, and a solid oxide electrolysis cell. Nitrogen is used as an inert carrier gas. The use of a carrier gas allows for independent variation of both the partial pressures and the flow rates of the steam and hydrogen gases while continuing to operate near atmospheric pressure. The flow rates of nitrogen, hydrogen and air are established by

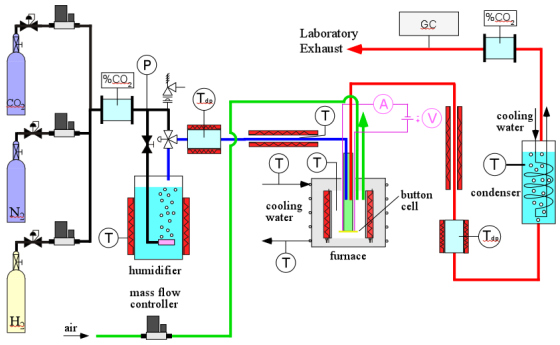

Figure 1. Schematic of INL electrolysis test apparatus.

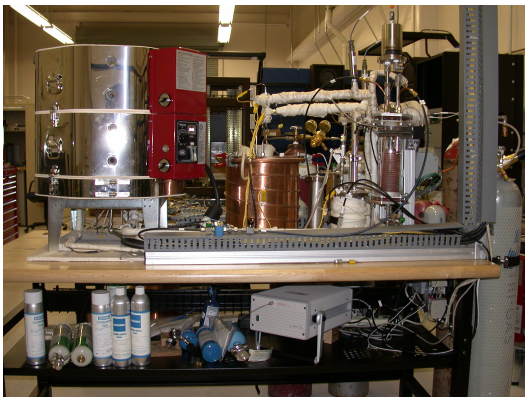

Figure 2. Photograph of INL electrolysis apparatus.

means of precision mass-flow controllers. Air flow to the stack is supplied by the shop air system, after passing through a two-stage extractor / dryer unit.

Downstream of the mass-flow controllers, nitrogen is mixed with a smaller flow of hydrogen gas and CO_2. Hydrogen is included in the inlet flow as a reducing gas in order to prevent oxidation of the Nickel cermet electrode material. The nitrogen/ hydrogen / CO_2 gas mixture is mixed with steam by means of a heated humidifier. The humidifier water temperature is maintained at a constant setpoint value using computerized feedback control. The dewpoint temperature of the nitrogen / hydrogen / CO_2 / steam gas mixture exiting the humidifier is monitored continuously using a precision dewpoint sensor. Pressure is also measured at the dewpoint measurement stations using absolute pressure transducers. Local stream pressure information is required to determine the mole fraction of steam in the gas mixture. These measurements have indicated that the dewpoint temperature of the gas mixture leaving the humidifier is very close to the water bath temperature, but not necessarily equal to it. Inlet CO_2 concentration is also monitored using a CO_2 sensor. Since the vapor pressure of the water and the resulting partial pressure of the steam exiting the humidifier are determined by the water bath temperature, the water vapor mass flow rate is directly proportional to the carrier gas flow rate for a specified bath temperature. Also, since the nitrogen, hydrogen, and CO_2 flow rates are fixed by the mass flow controllers, and the steam partial pressure is fixed by the bath temperature, the complete inlet gas composition is precisely known at all times. All gas lines located downstream of the humidifier are heat-traced in order to prevent steam condensation. Gas line temperatures are monitored by thermocouples and controlled by means of computer-controlled SCRs.

The inlet gas mixture is then directed to the high temperature furnace. The electrolyzer is heated and maintained at an appropriate operating temperature (800 to 830 C) via computer-based feedback control. The furnace also serves to preheat the inlet gas mixture and the air sweep gas. Oxygen produced by electrolysis is captured by the sweep gas stream and expelled into the laboratory. The syngas product stream is directed towards a second dewpoint sensor and CO_2 sensor upon exiting the furnace and then to a condenser through a heat-traced line. The condenser removes most of the residual steam from the exhaust. The final exhaust stream is vented outside the laboratory through the roof.

The rates of steam and CO_2 electrolysis are monitored by the measured change in inlet and outlet steam and CO_2 concentration as measured by the on-line sensors. In addition, a Gas Chromatograph has been incorporated into the facility to quantify the dry constituents in the electrolysis product stream (including any CH_4 that may be produced).

PROCESS AND MODEL DISCUSSION

The chemistry involved in the co-electrolysis of steam and CO_2 is significantly more complicated than steam electrolysis. There are three main competing processes occurring simultaneously. These are (in order of increasing kinetic rate) the electrolysis of CO_2 to CO, electrolysis of steam to H_2, and the reverse gas shift reaction:

$$CO_2 + H_2 \overset{k_{RSR}}{\Leftrightarrow} CO + H_2O \tag{2}$$

Where k_{rsr} is the reverse gas shift reaction equilibrium constant. One further electrolytic reaction that can occur if the cell potential is high enough is the conversion of CO to C, a situation that should be avoided since carbon deposits can hurt electrolysis cell performance. It is important to note that the electrolysis reactions are not equilibrium reactions in the sense that the electrolyte serves to partially separate products from reactants. However, the reverse gas shift reaction has reactants and products in equilibrium, with the desired syngas components of H_2 and CO as competing components. Furthermore, the reverse gas shift reaction equilibrium composition continues to change with gas stream temperature downstream from the electrolysis cell until the reaction kinetics freeze. Finally, at temperatures below 700 C, the catalytic (nickel) formation of methane may occur via internal reforming:

$$CO + 3H_2 \rightarrow CH_4 + H_2O. \tag{3}$$

In spite of the greater complexity of co-electrolysis versus electrolysing steam and CO_2 separately, there are inherent advantages to co-electrolysis for syngas production. For a given solid oxide electrolysis cell, CO_2 electrolysis will exhibit a higher area specific resistance (ASR) than steam electrolysis. This is due to the slower overall kinetics of CO_2 electrolysis, and higher overpotentials required, result in a higher ASR for a given electrolysis cell for CO_2 electrolysis than for steam electrolysis. In co-electrolysis, the reverse gas shift reaction is relied upon for most of the CO production and therefore the overall electrical requirement is less. Finally, in co-electrolysis the likelihood of producing carbon by electrolysis of CO is reduced.

To understand the impact of the three main processes discussed above, and to assist with interpretation of experimentally measured data, a co-electrolysis model was developed. This model also served to help determine the necessary inlet conditions for supporting experiments that were conducted. Using a correlation for the reverse gas shift reaction equilibrium constant as a function of gas temperature and the room temperature inlet gas molar composition, the model calculates the new equilibrium gas composition as the inlet gas mixture heats up to electrolysis conditions (800 to 830 C). The model then calculates an open-cell Nernst potential for this gas mixture. To account for electrolysis, the model first calculates the rate of oxygen transport from the syngas stream to the sweep gas stream:

$$\Delta n_O(I) = \frac{I}{2F} \tag{4}$$

where F is Faraday's constant and I is the electrolysis current. The model then solves the following set of 4 simultaneous equations:

$$n_{CO,inlet} + 2n_{CO_2,inlet} + n_{H_2O,inlet} = n_{CO,outlet} + 2n_{CO_2,outlet} + n_{H_2O,outlet} + \Delta n_O(I) \tag{5}$$

$$n_{CO,inlet} + n_{CO_2,inlet} = n_{CO,outlet} + n_{CO_2,outlet} \tag{6}$$

$$2n_{H_2,inlet} + 2n_{H_2O,inlet} = 2n_{H_2,outlet} + 2n_{H_2O,outlet} \tag{7}$$

$$k_{RSR}(T_{equil}) = \frac{n_{CO_2,outlet} n_{H_2,outlet}}{n_{CO,outlet} n_{H_2O,outlet}} \tag{8}$$

as a function of electrolysis current, where n represents moles of an element (C, O, etc.), and T_{equil} is the final cool down temperature at which the reverse gas shift reaction becomes kinetically frozen. This temperature was determined as follows. An experiment was run without any electrolysis (I = 0 amps). The same experimental inlet gas mixture composition was used in the above model. T_{equil} was varied in the model until the model predictions for outlet gas composition matched the measured results from the gas chromatograph. T_{equil} was found to be ~700 C. This

value for T_{equil} was then held constant for all subsequent model predictions. The model was then verified by comparing results with experimental results for various electrolysis current levels.

DISCUSSION OF RESULTS

Cell ASR is dependent upon the type of electrolysis being conducted. To illustrate this, an experiment was conducted where a button cell was used to electrolyze steam at 800°C. Without any change in operating temperature, the inlet gas to the cell was changed instantaneously from H_2/H_2O to CO/CO_2 and CO_2 electrolysis was conducted. The cell ASR value increased from 0.59 ohm-cm^2 to 0.90 ohm-cm^2 in response to the new gas composition.

To assess the feasibility of high temperature co-electrolysis for syngas production, as well as test the accuracy of the computer model described above, an inlet gas mixture comprised of 20.6% steam, 59.2% N_2, 6.7% H_2, and 13.5% CO_2 (74.5% N_2, 8.5% H_2, 17.0% CO_2 dry basis) was heated and electrolysed for a variety of electrical currents. The product gas stream was cooled to room temperature and any residual water removed before analysis by gas chromatography. The results are presented in Figure 3. As explained previously, the temperature at which the reverse gas shift reaction becomes kinetically frozen was 700 C. All model results used this value for T_{equil}.

At zero current, any change in composition is solely due to the reverse gas shift reaction. The CO_2 and H_2 compositions dropped by 2%, and CO was produced. As the electrolysis current was increased, the yield of syngas increased linearly while the concentration of CO_2 decreased. The ratio of H_2 to CO dropped slightly from 3 to 2.6 as the electrolysis current was increased from 0 to 0.73 amps. Electrolysis of steam to produce H_2 forces the reverse shift gas reaction equilibrium in Eq. 2 to the right, consuming H_2 and CO_2 while producing CO. There was no experimental evidence of internal reforming occurring. Model predictions agree very well with the experimental measurements. Future research plans include further model validation via co-electrolysis experiments at a variety of inlet compositions and electrolysis temperatures, long duration co-electrolysis tests, and limited larger-scale co-electrolysis tests involving solid oxide cell stacks.

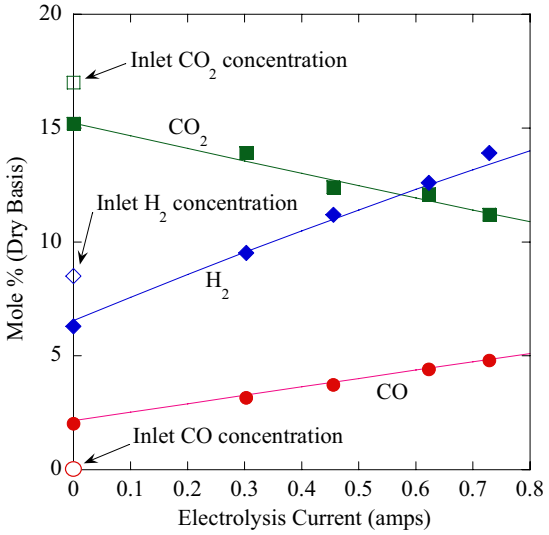

Figure 3. Comparison of model (lines) and experimental (symbols) results.